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by

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COMPARISON OF IRRADIATION DAMAGE IN ARTIFICIAL AND NATURAL GRAPHITE AT DIFFERENT IRRADIATION TEMPERATURES

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Abstract — Résumé — Аннотация — Resumen

COMPARISON OF IRRADIATION DAMAGE IN ARTIFICIAL AND NATURAL GRAPHITE AT DIFFERENT IRRADIATION TEMPERATURES. Results of irradiation experiments on artificial and natural graphite in the three temperature ranges 70 - 150°C, 300 - 400°C and 550 - 650°C are compared. These irradiation experiments were carried out in core or pool positions of the GETR, Vallecitos. The samples investigated received neutron doses up to 5×10^{21} nvt with E > 0.17 eV, which is approximately 3×10^{21} nvt with E > 0.18 MeV. Changes in the lattice parameters, the electric and thermal conductivity, the macroscopic dimensions and the bending strength are discussed. The natural graphite samples investigated were manufactured partly with, partly without a binding material. The results obtained during these investigations indicate, in addition to the dependence on the irradiation temperature and the neutron dose, a strong influence exerted by the basic materials, the treatment during production and the density. Strong anisotropic effects in natural graphite at lower irradiation temperatures, resulting from the treatment during production, level out at higher irradiation temperatures.

COMPARAISON DES DOMMAGES SUBIS PAR DES GRAPHITES ARTIFICIELS ET NATURELS IRRADIÉS A DES TEMPÉRATURES DIFFÉRENTES. L'auteur compare les résultats d'expériences consistant à exposer du graphite artificiel et naturel à un flux de neutrons, à des températures comprises dans les trois gammes suivantes: 70 - 150°C, 300 - 400°C et 550 - 650°C. Ces expériences ont eu lieu tant à l'intérieur qu'à l'extérieur du cœur du réacteur GETR de Vallecitos. Les échantillons étudiés ont reçu des doses allant jusqu'à $5 \cdot 10^{21}$ nvt avec une énergie de E > 0,17 eV, ce qui correspond à environ $3 \cdot 10^{21}$ nvt avec E > 0,18 MeV. L'auteur discute les modifications observées dans les paramètres de réseau, la conductivité électrique et thermique, les dimensions macroscopiques et la flexibilité. Les échantillons de graphite naturel considérés avaient été fabriqués en partie à l'aide d'une substance liante et en partie sans une telle substance. Il ressort de ces expériences que les résultats varient non seulement avec la température d'irradiation et la dose de neutrons mais qu'ils sont déterminés dans une forte mesure par les matériaux de base, le traitement au cours de la fabrication et la densité. Les effets anisotropiques considérables qu'on observe dans le graphite naturel à des températures d'irradiation relativement peu élevées et qui résultent du traitement au cours de la fabrication, s'atténuent graduellement lorsque la température d'irradiation augmente.

СРАВНЕНИЕ РАДИАЦИОННЫХ ПОВРЕЖДЕНИЙ В ИСКУСТВЕННОМ И ПРИРОДНОМ ГРАФИТЕ ПРИ РАЗЛИЧНЫХ ТЕМПЕРАТУРАХ ВО ВРЕМЯ ОБЛУЧЕНИЯ. Сравниваются результаты опытов облучения искуственного и природного графита при температурах в пределах от 70 до 150°C, от 300 до 400°C и от 550 до 650°C. Опыты производились в активной зоне или в бассейне реактора GETR в Вальлеситосе. Обследованные образцы были подвергнуты воздействию доз нейтронов до $5 \cdot 10^{21}$ nvt при E > 0,17 Мэв, что соответствует приблизительно $3 \cdot 10^{21}$ nvt при E > 0,18 Мэв. Обсуждаются изменения параметров решетки, электропроводимости и теплопроводности, микроскопических размеров и сопротивления на изгиб. Изученные образцы природного графита были изготовлены частью со связующим материалом, а частью без него. Полученные при этих исследованиях результаты показывают, что, помимо зависимости от температуры при облучении и от дозы нейтронов, имеет место также сильная зависимость от исходных материалов, обработки во время изготовления и плотности. Сильное анизотропное воздействие в природном графите при более низких температурах во время облучения, возникающее в результате обработки в процессе производства, выравнивается при облучении при более высоких температурах.

COMPARACIÓN ENTRE LOS DAÑOS CAUSADOS POR LAS RADIACIONES EN GRAFITOS ARTIFICIALES Y NATURALES POR IRRADIACION A DIVERSAS TEMPERATURAS. La memoria compara los resultados de experimentos de irradiación de grafito artificial y natural en tres intervalos de temperatura que abarcan de 70 - 150°C, de 300 - 400°C y de 550 - 650°C, respectivamente. Los experimentos se efectuaron en el cuerpo o en el tanque del reactor GETR de Vallecitos. Las muestras investigadas recibieron dosis neutrónicas de hasta $5 \cdot 10^{21}$ nvt, con $E > 0,17$ eV, lo que corresponde aproximadamente a $3 \cdot 10^{21}$ nvt, con $E > 0,18$ MeV. La memoria discute las alteraciones sufridas por los parámetros de la red cristalina, la conductividad eléctrica y térmica, las dimensiones macroscopicas y la resistencia a la flexion. Las muestras de grafito natural investigadas fueron preparadas en parte con material aglomerante y en parte sin él. Los resultados obtenidos durante estas investigaciones indican que, además de la temperatura de irradiación y de la dosis neutrónica, las materias primas, el tratamiento recibido durante la elaboración y la densidad ejercen una influencia muy marcada. Los fuertes efectos anisotrópicos que aparecen en el grafito natural a reducidas temperaturas de irradiación, y que son resultado del tratamiento durante la elaboración,quedan compensados al irradiar a temperaturas más elevadas.

1. INTRODUCTION

Graphite is used extensively in nuclear reactors both as a moderator and as a structural material and it also plays a particularly important part in the design of high-temperature reactors. Apart from acting as a moderator or reflector, it is used as a canning material and in most cases replaces the normal metallic canning for fuel elements.

Apart from the nuclear purity and the fulfilment of the physical and technical properties required at normal operating temperatures, there are additional demands for a very low permeability in order to keep the diffusion rate of gaseous fission products low.

As early as 1955 it was pointed out [1] that, because of its high density, natural graphite could have considerable advantages in reactor-construction applications. While the apparent density of artificial graphite is normally between 1.6 g/cm³ and 1.7 g/cm³ and much higher densities can only be achieved by expensive impregnation processes, apparent densities of more than 2.0 g/cm³ are easily obtained with natural graphite: because of the higher density and the resultant better neutron moderation, savings in core volume and construction costs could be expected.

Unfortunately, at that time, the mechanical properties of moulded natural-graphite blocks without any binding material were not sufficient to justify its use in reactor construction, especially at normal operating temperatures. Moreover, because of the high density and considerable anisotropy of the die-moulded blocks, larger amounts of irradiation damage were expected at ambient temperatures. Hence this material has had only limited use, e.g. for thermal columns in research reactors.

Since that time the properties of natural graphite have been improved by the use of appropriate binding materials [2] and the possibility of using this material in high-temperature reactors and as a canning material has, as a result, become more interesting. As the apparent density is close to 2.0 g/cm³, this graphite has, because of its dense texture, a primary permeability of about 10^{-3} cm²/sec. This can be brought to a permeability of better than 10^{-7} cm²/sec by a simple and economical procedure.

The investigation described below was carried out in order to obtain information on the behaviour of natural-graphite samples under reactor irradiation at different temperatures.

2. INVESTIGATION OF GRAPHITE GRADES

Two grades of natural graphite were irradiated. Both were die-moulded into blocks, grade A without any binder, grade B using formaldehyde resins as a binder. Because of the disc form of the crystallites, they become preferentially orientated during the moulding with the c-axis parallel to the direction of pressure.

In order to compare the results of these experiments with the damage induced in a representative artificial graphite, samples of CSF graphite were also irradiated. This grade and its property changes under neutron irradiation have been extensively investigated by many authors, e.g. [3-10].

Artificial graphite generally will be extruded during production. In such a case, therefore, the c-axis of the crystallites is preferentially orientated perpendicular to the direction of pressure. Samples with their axes in some cases perpendicular and in others parallel to the direction of pressure were cut out of the moulded blocks. Because of the different method of manufacture parallel (||) samples of this natural graphite correspond to the perpendicular (⊥) samples of CSF graphite and vice versa.

Table I lists the properties of the samples investigated before irradiation. Irradiations were carried out in pool or core positions of the GETR* reactor. The fast-neutron dose-value was obtained using sulphur monitors and theoretical calculations, applying the three-group treatment. As the group with the highest energy lay above 0.18 MeV, we used this group to measure the neutron dose. There is reason to believe that irradiation damage in graphite will be induced mainly by neutrons having a threshold energy of at least 0.1 MeV.

Discrepancies between the calculated and measured neutron dose are of minor importance in this case, as the samples compared with each other at the same temperature were always placed in the same capsule. During irradiation the recorded temperature showed some oscillations introduced by fluctuations in reactor operation. The data given in the figures are best averages, the temperature dependence of irradiation damage being taken into account.

3. CRYSTALLITE PROPERTIES

The crystallite changes in the c- and a-spacing induced in graphite by irradiation were studied by X-ray diffraction techniques using the (002) and (110) reflections. While there is no noticeable difference in the a_0-spacing of the three grades investigated before irradiation (Table I), the c_0-spacing shows the expected variations. Samples containing more perfect crystallites (natural graphite) have a smaller lattice spacing. In Figs. 1 and 2, changes of the lattice parameters are plotted against the irradiation temperature

* GETR: General Electric Test Reactor, Vallecitos Atomic Laboratory, California.

TABLE I

PROPERTIES OF GRAPHITE
(Average, unirradiated)

	CSF	A	B
Type	Artificial graphite Petrol-coke, extruded	Natural graphite moulded blocks	Natural graphite moulded blocks
Binder	coal tar pitch	none	phenol-formaldehyde resins
Apparent density (g/cm^3)	1.66	2.07	1.97
Thermal conductivity ($cal\ cm^{-1}\ sec^{-1}\ °C^{-1}$)	0.32 $\perp$ 0	0.55 $\perp$ 0.08 $\parallel$	0.30 $\perp$ 0.09 $\parallel$
Electrical resistivity ($\Omega mm^2\ m^{-1}$)	12 $\perp$	5.2 $\perp$ 45 $\parallel$	9.1 $\perp$ 32 $\parallel$
c_0 spacing (Å)	6.732	6.715	6.715
a_0 spacing (Å)	2.461	2.461	2.461

for neutron doses of 7.5×10^{19} and $4.5 \times 10^{20}\ n/cm^2$, $E > 0.18$ MeV, respectively. The strong increase of the c-spacing at ambient temperatures is much less marked for exposure at higher temperatures. At 500°C the change of this lattice parameter has already decreased to only 0.1 to 0.2%. Within the accuracy of measurement, all graphite grades investigated show the same relative changes.

This small increase in the c-spacing indicates that no single interstitial is stable under these conditions. Because of the high thermal energy, their mobility is high enough to effect recombination with vacancies. The measured increase in the c-spacing should therefore, as assumed by HENNIG and HOVE [11], result from complexes or clusters of carbon atoms or from molecules.

There is also a relatively high contraction in the direction of the a-axes, which is the same for all investigated grades. Though it is difficult to give

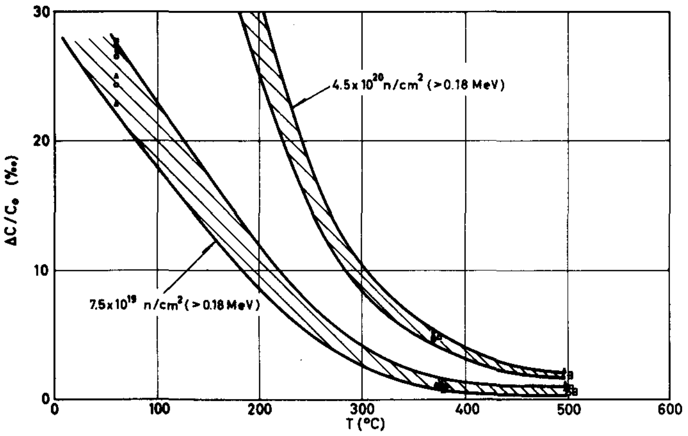

Fig. 1

Variation of c_0-spacing with exposure temperature

○ CSF ⊥   ▲ A ‖

△ A ⊥   ■ B ‖

□ B ⊥

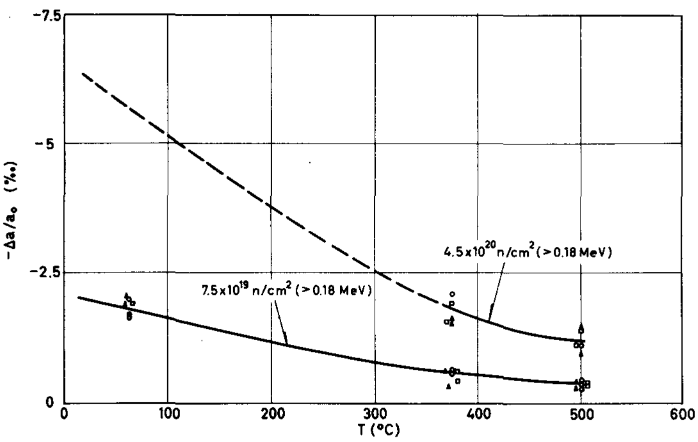

Fig. 2

Variation of a_0-spacing with exposure temperature

○ CSF ⊥   ▲ A ‖

△ A ⊥   ■ B ‖

□ B ⊥

quantitative statements, it is believed that this high amount cannot only be attributed to buckling of the planes. Also the assumed production of dislocations [11], most likely formed when displaced atoms try to re-integrate into the lattice, must contribute to this effect.

4. DIMENSIONAL CHANGES

Because of the strong anisotropy of the graphite bodies, the samples cut out in the two main directions also show very different changes in length (Figs. 3 and 4). The increase of the c-spacing is essentially responsible for this; a smaller or larger proportion of the crystallite expansion takes place parallel to the sample axis, depending on the degree of anisotropy. At 500°C this increase is not yet compensated by the crystallite contractions in the direction of the a-axis.

The higher the density of a graphite grade, the more the crystallite growth contributes to the macroscopic length changes, as less pore volume is available for filling out by the expanding crystallites.

At 500°C the bound natural graphite (grade B) shows the same length change as the CSF graphite. By a comparison of Figs. 1 to 4, one can see that the macroscopic length changes of grade A (without binders) are in some cases larger than the increases in the crystallite dimensions. We attribute this to irreversible processes produced by thermal cycling during irradiation which cause a loosening of the texture.

5. ELECTRICAL RESISTIVITY

It is well known from the literature that the electrical resistivity of irradiated graphite approaches a saturation value at a relatively low neutron dose. This fact is also indicated by Figs. 5 and 6. Though the neutron dose in Fig. 5 is higher by a factor of six than in Fig. 6, there is only little difference in the resistivity changes of the same samples. But there is a linear decrease in the resistivity change with increasing temperature at a certain neutron dose.

In this case the relative changes ρ/ρ_0 for the grades A and B seem to be more favourable than for CSF. As these are only relative values (referred to the resistivity of each grade and cut before irradiation), one has to apply the original data given in Table I in order to obtain absolute values.

6. THERMAL CONDUCTIVITY

The behaviour of the thermal conductivity of graphite under neutron irradiation plays an important part in reactor design. In this case also, the curves of the graphite grades investigated converge strongly at 500°C (Figs. 7 and 8). The relative values λ/λ_0 are again below those of CSF graphite at this point. In order to get the absolute values of the thermal conductivity, one again has to use the original data before irradiation, given in Table I.

7. BENDING STRENGTH

The variation of the bending strength (transverse breaking strength) is plotted in Figs. 9 and 10 against the irradiation temperature for neutron doses of 7.5×10^{19} and 4.5×10^{20} n/cm², E > 0.18 MeV, respectively. The graphite samples, which were of 5-mm square cross-section, were laid on blunt edges 40 mm apart. The load was applied in the middle of the

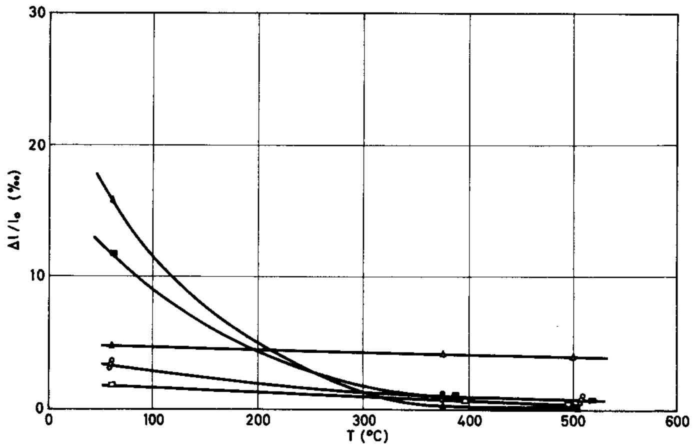

Fig. 3

Effects of temperature on physical expansion
(Exposure to 7.5 × 10^{19} n/cm^2 with energies > 0.18 MeV)

○ CSF ⊥ ▲ A ∥
△ A ⊥ ■ B ∥
□ B ⊥

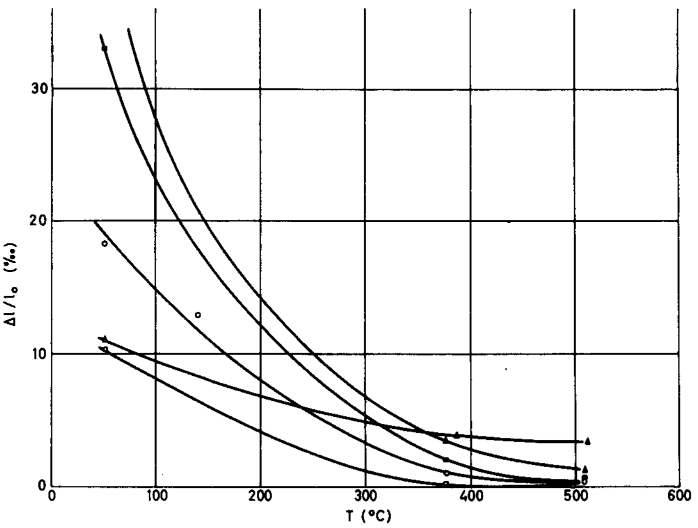

Fig. 4

Effects of temperature on physical expansion
(Exposure to 4.5 × 10^{20} n/cm^2 with energies > 0.18 MeV)

○ CSF ⊥ ▲ A ∥
△ A ⊥ ■ B ∥
□ B ⊥

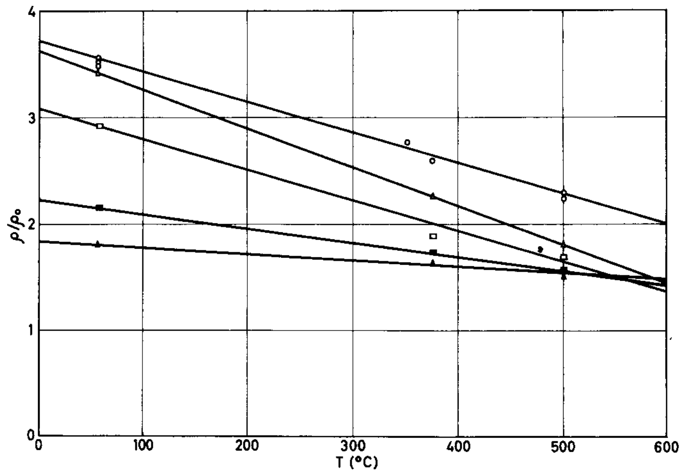

Fig. 5

Variation in electrical resistivity with irradiation temperature
(Exposure 7.5 × 10^{19} n/cm^2 with energies > 0.18 MeV)

○ CSF ⊥ ▲ A ∥

△ A ⊥ ■ B ∥

□ B ⊥

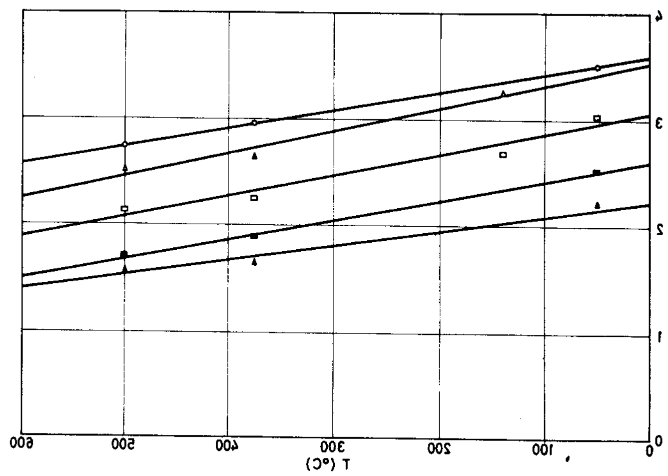

Fig. 6

Variation in electrical resistivity with irradiation temperature
(Exposure 4.5 × 10^{20} n/cm^2 with energies > 0.18 MeV)

○ CSF ⊥ ▲ A ∥

△ A ⊥ ■ B ∥

□ B ⊥

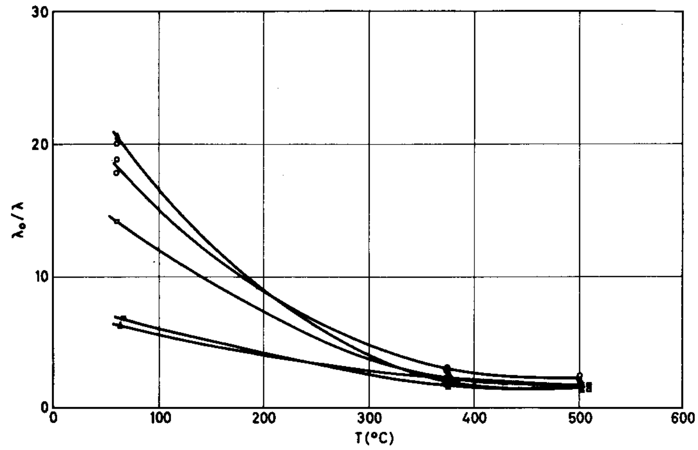

Fig. 7

Variation in thermal conductivity with irradiation temperature
(Exposure 7.5×10^{19} n/cm² with energies > 0.18 MeV)

○ CSF ⊥ ▲ A ∥
△ A ⊥ ■ B ∥
□ B ⊥

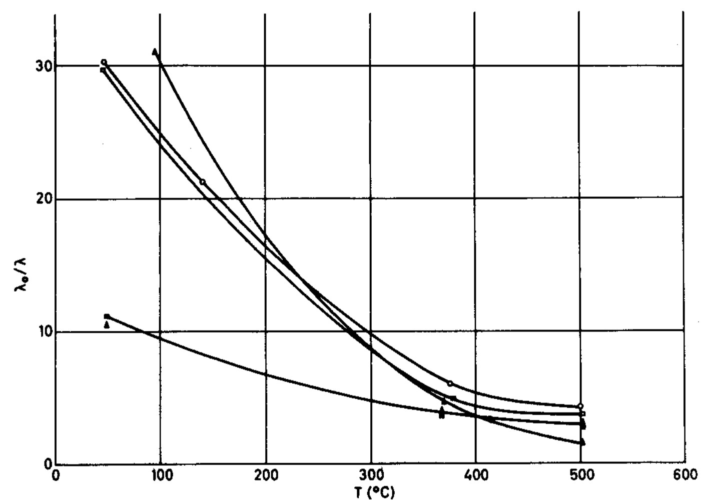

Fig. 8

Variation in thermal conductivity with irradiation temperature
(Exposure 4.5×10^{20} n/cm² with energies > 0.18 MeV)

○ CSF ⊥ ▲ A ∥
△ A ⊥ ■ B ∥
□ B ⊥

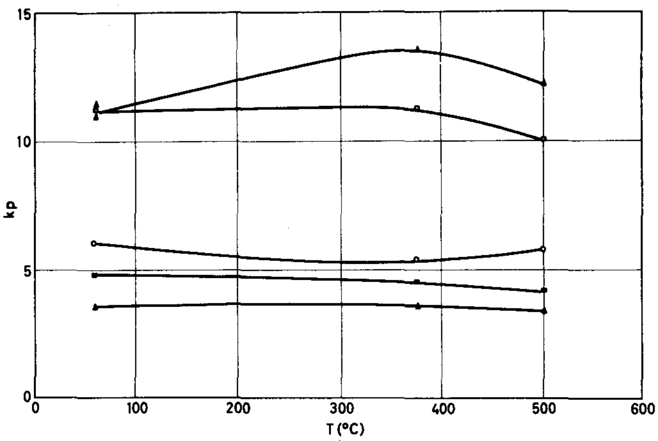

Fig. 9

Changes in bending strength with irradiation temperature
(Exposure 7.5×10^{19} n/cm^2 with energies > 0.18 MeV, 5mm square sample)

○ CSF ⊥ ▲ A ∥
△ A ⊥ ■ B ∥
□ B ⊥

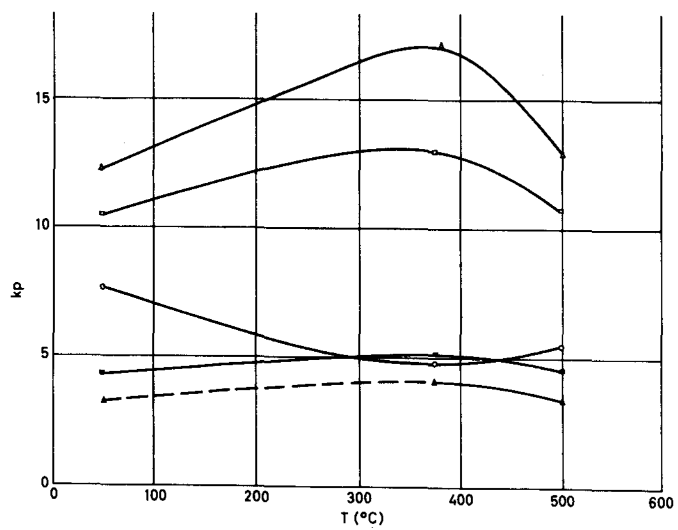

Fig. 10

Changes in bending strength with irradiation temperature
(Exposure 4.5×10^{20} n/cm^2 with energies > 0.18 MeV, 5-mm square sample)

○ CSF ⊥ ▲ A ∥
△ A ⊥ ■ B ∥
□ B ⊥

sample through a 10-mm radius, cylindrical section. Because of inevitable notch effects resulting from small cracks or larger pores, the values obtained cannot be converted to the commonly used unit kp*/cm^2. Much smaller values are found in 5-mm square samples as compared with those resulting from 10-mm square samples. Therefore the numbers on the ordinates of the graphs give only a relative measure.

Again these figures indicate the considerable difference in the bending strength in both directions, caused by the strong anisotropy. While both perpendicular-cut natural graphite samples have a very high bending strength, the values of the A(‖) and B(‖) samples are a little below those of CSF.

The nature of the bending strength against irradiation temperature curve is very interesting. Whereas all natural graphite curves are convex, those of CSF graphite are concave. Two competing effects seem to overlap. It is assumed that at first (lower-temperature condition) there is an increase in strength due to the formation of bridges between neighbouring grains. The easily-mobile groups of interstitials must be responsible for this effect, some of which migrate to the grain boundaries and form the connexion. At higher temperatures the rate of production of groups of interstitials becomes less and less because of the high rate of recombination. This may explain the falling portion of the bending-strength curve. The diffusion of vacancies to the grain boundary, where they are able to form small pores and thus loosen the texture, must be of minor importance in this temperature range. As the average crystallite or grain size is much higher in natural graphite than in artificial graphite, this initial increase and subsequent decrease in bending strength should occur strongly here, the more so since there is very little pore volume at the beginning. This effect is greater in natural graphite without binder, as would be expected.

8. CONCLUSIONS

The investigations carried out on these graphite grades show clearly the limitations and possibilities of moulded natural graphite in reactor construction.

At ambient irradiation temperatures, due to the strong anisotropy of the moulded blocks and because of their high density, dimension changes are already so considerable that even a relatively low neutron dose of about 10^{19} n/cm^2, $E > 0.18$ MeV is not tolerable.

These high damage rates increasingly disappear with rising irradiation temperature. By about 500°C all property changes investigated are of the same magnitude as those of CSF graphite. There is also very little difference in the strength factors. Therefore in this temperature region the use of natural-graphite grades in reactor construction should be possible at the present stage of development. Compared with the commonly used artificial graphite, the higher density and lower permeability should also be advantageous.

* kp: kilo-pond or kilogram weight.

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